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INTERNATIONAL PRELIMINARY EXAMINATION REPORT
(PCT Article 36 and Rule 70)

Applicant's or agent's file reference P28788PC00	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEA/416)
International application No. PCT/ZA 03/00186	International filing date (day/month/year) 19.12.2003	Priority date (day/month/year) 20.12.2002
International Patent Classification (IPC) or both national classification and IPC B01J31/18		
Applicant SASOL TECHNOLOGY (PTY) LIMITED et al.		

<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 4 sheets, including this cover sheet.</p> <p><input checked="" type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of 22 sheets.</p>
<p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> I <input checked="" type="checkbox"/> Basis of the opinion II <input type="checkbox"/> Priority III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability IV <input type="checkbox"/> Lack of unity of invention V <input checked="" type="checkbox"/> Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement VI <input type="checkbox"/> Certain documents cited VII <input type="checkbox"/> Certain defects in the international application VIII <input type="checkbox"/> Certain observations on the international application

Date of submission of the demand 18.05.2004	Date of completion of this report 07.04.2005
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**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/ZA 03/00186

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, Pages

1-4, 6-11, 13-19, 30	as originally filed
5, 12, 20-29	filed with telefax on 12.10.2004

Claims, Numbers

1-57	received on 16.03.2005 with letter of 16.02.2005
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2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- the language of publication of the international application (under Rule 48.3(b)).
- the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- contained in the international application in written form.
- filed together with the international application in computer readable form.
- furnished subsequently to this Authority in written form.
- furnished subsequently to this Authority in computer readable form.
- The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- the description, pages:
- the claims, Nos.:
- the drawings, sheets:

5. This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

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**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability;
citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes:	Claims	-
	No:	Claims	1-57
Inventive step (IS)	Yes:	Claims	-
	No:	Claims	1-57
Industrial applicability (IA)	Yes:	Claims	1-57
	No:	Claims	

2. Citations and explanations

see separate sheet

**INTERNATIONAL PRELIMINARY
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International application No. PCT/ZA 03/00186

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

The embodiment described in dependent claim 19 and in the description on page 6 last paragraph to page 7 first paragraph does either not fall within the scope of claim 1, or claim 1 is not new over D2.

If the condition formulated in first paragraph of claim 1 (at least one R is substituted with a polar substituent) is valid for all heteroatomic ligands (falling under formula I or II of the present set of claims) there exists an inconsistency between the claims and the description (see above cited passage), which leads to doubt concerning the matter for which protection is sought, thereby rendering the claims unclear, Article 6 PCT.

If not, the present application is not new over D2:

D2: WO 02/04119

Claim 27 discloses a process for the oligomerization of olefines in the presence of a catalyst as defined in claim 1-25.

Claim 10 discloses catalyst composition comprising a transition metal compound (chromium, molybdenum tungsten) in the presence of $R_1R_2XYR_3R_4$ where R1-R4 can be selected from: methoxy, ethoxy, phenoxy,.... X is phosphor , arsenic or antimony and y is a bridging group.

(compare with claim 19 of the present application)

Therefore the subject matter of the independent claims 1, and 33 is not new over D2.

RPM's using a gas entraining stirrer. The reaction was terminated after 15 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 1.2060 g of polyethylene. The GC analyses indicated that the reaction mixture contained 81.51 g oligomers. The product distribution of this example is summarised in Table 1.

Example 16: Ethylene tetramerisation reaction using Cr (III) acetylacetonoate, (phenyl)₂PN(isopropyl)P(2-methoxyphenyl)₂ and MAO

A solution of 32.2 mg of (phenyl)₂PN(isopropyl)P(2-methoxyphenyl)₂ (0.066 mmol) in 10 ml of toluene was added to a solution of 1.5 mg chromium (III) acetylacetonoate (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane in toluene, 4.5 mmol) at 40°C. The pressure reactor was first charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 45 barg. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 15 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 6.82 g of polyethylene. The GC analyses indicated that the reaction mixture contained 38.33 g oligomers. The product distribution of this example is summarised in Table 1.

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Example 14: Ethylene tetramerisation reaction using Cr (III) acetylacetonoate, (4-methoxyphenyl)₂PN(isopropyl)P(4-methoxyphenyl)₂ and EAO/TMA

A solution of 36.1 mg of (4-methoxyphenyl)₂PN(isopropyl)P(4-methoxyphenyl)₂ (0.066 mmol) in 10 ml of toluene was added to a solution of 5.2 mg chromium (III) acetylacetonoate (0.015 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml), EAO (ethylaluminoxane in toluene, 33 mmol) and TMA (trimethylaluminium, 8.25mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 45 barg. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 60 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 0.189 g of polyethylene. The GC analyses indicated that the reaction mixture contained 40.97g oligomers. The product distribution of this example is summarised in Table 1.

Example 15: Ethylene tetramerisation reaction using Cr (III) acetylacetonoate, (4-methoxyphenyl)₂PN(isopropyl)P(4-methoxyphenyl)₂ and MAO in the presence of H₂

A solution of 16.4 mg of (4-methoxyphenyl)₂PN(isopropyl)P(4-methoxyphenyl)₂ (0.03 mmol) in 10 ml of toluene was added to a solution of 5.2 mg chromium (III) acetylacetonoate (0.015 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane in toluene, 4.5 mmol) at 40°C. The pressure reactor was first charged with hydrogen to a pressure of approximately 2.5 barg and subsequently with ethylene to 45 barg after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 45 barg. Thorough mixing was ensured throughout by mixing speeds of 1100

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discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 0.5010 g of polyethylene. The GC analyses indicated that the reaction mixture contained 70.87 g oligomers. The product distribution of this example is summarised in Table 1.

Example 13: Ethylene tetramerisation reaction using Cr (III) acetylacetonoate, (4-methoxyphenyl)₂PN(isopropyl)P(4-methoxyphenyl)₂ and MMAO-3A

A solution of 16.4 mg of (4-methoxyphenyl)₂PN(isopropyl)P(4-methoxyphenyl)₂ (0.03 mmol) in 10 ml of toluene was added to a solution of 5.2 mg chromium (III) acetylacetonoate (0.015 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MMAO-3A (modified methylaluminoxane in heptanes, 4.5 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 45 barg. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 22 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 1.76 g of polyethylene. The GC analyses indicated that the reaction mixture contained 50.42g oligomers. The product distribution of this example is summarised in Table 1.

Example 11: Ethylene tetramerisation reaction using Cr (III) acetylacetonoate, (4-methoxyphenyl)₂PN(isopropyl)P(4-methoxyphenyl)₂ and MAO

A solution of 6.6 mg of (4-methoxyphenyl)₂PN(isopropyl)P(4-methoxyphenyl)₂ (0.012 mmol) in 10 ml of toluene was added to a solution of 3.5 mg chromium (III) acetylacetonoate (0.015 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 3.0 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 45 barg. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 30 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 1.3958 g of polyethylene. The GC analyses indicated that the reaction mixture contained 54.52 g oligomers. The product distribution of this example is summarised in Table 1.

Example 12: Ethylene tetramerisation reaction using Cr (III) acetylacetonoate, (4-methoxyphenyl)₂PN(isopropyl)P(4-methoxyphenyl)₂ and MAO

A solution of 9.8 mg of (4-methoxyphenyl)₂PN(isopropyl)P(4-methoxyphenyl)₂ (0.018 mmol) in 10 ml of toluene was added to a solution of 5.2 mg chromium (III) acetylacetonoate (0.015 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane in toluene, 2.25 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 45 barg. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 15 minutes by

30 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 1.52 g of polyethylene. The GC analyses indicated that the reaction mixture contained 61.27 g oligomers. The product distribution of this example is summarised in Table 1.

Example 10: Ethylene tetramerisation reaction using Cr (III) octanoate , (4-methoxyphenyl)₂PN(isopropyl)P(4-methoxyphenyl)₂ and MAO

A solution of 9.8 mg of (4-methoxyphenyl)₂PN(isopropyl)P(4-methoxyphenyl)₂ (0.018 mmol) in 10 ml of toluene was added to a solution of 10.3 mg Cr (III) octanoate (70% in toluene, 0.015 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 4.5 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 45 barg. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 40 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 0.3773 g of polyethylene. The GC analyses indicated that the reaction mixture contained 18.91 g oligomers. The product distribution of this example is summarised in Table 1.

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Example 8: Ethylene tetramerisation reaction using CrCl₃.THF₃, (4-methoxyphenyl)₂PN(isopropyl)P(4-methoxyphenyl)₂ and MAO

A solution of 9.8 mg of (4-methoxyphenyl)₂PN(isopropyl)P(4-methoxyphenyl)₂ (0.018 mmol) in 10 ml of toluene was added to a solution of 5.6 mg CrCl₃.THF₃ (0.015 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 4.5 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 45 barg. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 30 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 1.0831 g of polyethylene. The GC analyses indicated that the reaction mixture contained 42.72 g oligomers. The product distribution of this example is summarised in Table 1.

Example 9: Ethylene tetramerisation reaction using Cr (III) 2-ethylhexanoate, (4-methoxyphenyl)₂PN(isopropyl)P(4-methoxyphenyl)₂ and MAO

A solution of 9.8 mg of (4-methoxyphenyl)₂PN(isopropyl)P(4-methoxyphenyl)₂ (0.018 mmol) in 10 ml of toluene was added to a solution of 10.2 mg Cr (III) 2-ethylhexanoate (70% in mineral oil, 0.015 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 4.5 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 45 barg. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after

ethylene pressure was kept at 45 barg. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 11 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 1.9168 g of polyethylene. The GC analyses indicated that the reaction mixture contained 62.72g oligomers. The product distribution of this example is summarised in Table 1.

Example 7: Ethylene tetramerisation reaction using Cr (III) acetylacetonoate, (4-methoxyphenyl)₂PN(isopropyl)P(4-methoxyphenyl)₂ and MAO

A solution of 9.8 mg of (4-methoxyphenyl)₂PN(isopropyl)P(4-methoxyphenyl)₂ (0.018 mmol) in 10 ml of toluene was added to a solution of 5.2 mg chromium (III) acetylacetonoate (0.015 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 4.5 mmol) at -40°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 45 barg. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 21 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 0.8280 g of polyethylene. The GC analyses indicated that the reaction mixture contained 69.17 g oligomers. The product distribution of this example is summarised in Table 1.

that the reaction mixture contained 61.33g oligomers. The product distribution of this example is summarised in Table 1.

Example 5: Ethylene tetramerisation reaction using Cr (III) acetylacetonoate, (4-methoxyphenyl)₂PN(isopropyl)P(4-methoxyphenyl)₂ and MAO

A solution of 36.1 mg of (4-methoxyphenyl)₂PN(isopropyl)P(4-methoxyphenyl)₂ (0.066 mmol) in 10 ml of toluene was added to a solution of 11.5 mg chromium (III) acetylacetonoate (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor, (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 45 barg. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 12 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 2.3010 g of polyethylene. The GC analyses indicated that the reaction mixture contained 73.53g oligomers. The product distribution of this example is summarised in Table 1.

Example 6: Ethylene tetramerisation reaction using Cr (III) acetylacetonoate, (4-methoxyphenyl)₂PN(isopropyl)P(4-methoxyphenyl)₂ and MAO

A solution of 16.4 mg of (4-methoxyphenyl)₂PN(isopropyl)P(4-methoxyphenyl)₂ (0.03 mmol) in 10 ml of cyclohexane was added to a solution of 5.2 mg chromium (III) acetylacetonoate (0.015 mmol) in 10 ml cyclohexane in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of cyclohexane (80ml) and MAO (methylaluminoxane in toluene, 4.5 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the

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(methylaluminoxane, 9.9 mmol) at 60°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 65°C, while the ethylene pressure was kept at 30 barg. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 30 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 1.2269 g of polyethylene. The GC analyses indicated that the reaction mixture contained 9.71g oligomers. The product distribution of this example is summarised in Table 1.

Example 4: Ethylene tetramerisation reaction using Cr (III) acetylacetonate, (4-methoxyphenyl)₂PN(isopropyl)P(4-methoxyphenyl)₂ and MAO

A solution of 36.1 mg of (4-methoxyphenyl)₂PN(isopropyl)P(4-methoxyphenyl)₂ (0.066 mmol) in 10 ml of toluene was added to a solution of 11.5 mg chromium (III) acetylacetonate (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 60°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 65°C, while the ethylene pressure was kept at 30 barg. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 30 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 0.7105 g of polyethylene. The GC analyses indicated

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which the ice bath was removed. After stirring for a total of 14 hrs the solution was filtered to remove the triethylammonium salt formed. The product was isolated after crystallisation in a 77 % yield. ^{31}P {H} NMR: 47.4 ppm (broad singlet)

Example 2: Ethylene tetramerisation reaction using Cr (III) acetylacetonoate, (4-methoxyphenyl)₂PN(methyl)P(4-methoxyphenyl)₂ and MAO

A solution of 30.0 mg of (4-methoxyphenyl)₂PN(methyl)P(4-methoxyphenyl)₂ (0.066 mmol) in 10 ml of toluene was added to a solution of 11.5 mg chromium (III) acetylacetonoate (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 60°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 65°C, while the ethylene pressure was kept at 30 barg. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 30 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 0.2254 g of polyethylene. The GC analyses indicated that the reaction mixture contained 38.50g oligomers. The product distribution of this example is summarised in Table 1.

Example 3: Ethylene tetramerisation reaction using Cr (III) acetylacetonoate, (3-methoxyphenyl)₂PN(methyl)P(3-methoxyphenyl)₂ and MAO

A solution of 30.0 mg of (3-methoxyphenyl)₂PN(methyl)P(3-methoxyphenyl)₂ (0.066 mmol) in 10 ml of toluene was added to a solution of 11.5 mg chromium (III) acetylacetonoate (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO.

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the presence or absence of an inert solvent, and/or by slurry reaction where the catalyst system is in a form that displays little or no solubility, and/or a two-phase liquid/liquid reaction, and/or a bulk phase reaction in which neat reagent and/or product olefins serve as the dominant medium, and/or gas phase reaction, using conventional equipment and contacting techniques.

The process may therefore also be carried out in an inert solvent. Any inert solvent that does not react with the activator can be used. These inert solvents may include any saturated aliphatic and unsaturated aliphatic and aromatic hydrocarbon and halogenated hydrocarbon. Typical solvents include, but are not limited to, benzene, toluene, xylene, cumene, heptane, methylcyclohexane, methylcyclopentane, cyclohexane, 1-hexene, 1-octene, ionic liquids and the like.

The process may be carried out at pressures from atmospheric to 500 barg. Ethylene pressures in the range of 10-70 barg are preferred. Particularly preferred pressures range from 30-50 barg.

The process may be carried out at temperatures from - 20 °C - 250 °C. Temperatures in the range of 15-130 °C are preferred. Particularly preferred temperatures range from 35-100°C.

In a preferred embodiment of the invention, the heteroatomic coordination complex and reaction conditions are selected such that the yield of 1-octene from ethylene is greater than 30 mass %, preferably greater than 35 mass %. In this regard yield refers to grams of 1-octene formed per 100g of total reaction product formed.

In addition to 1-octene, the process may also yield different quantities of 1-butene, 1-hexene, methylcyclopentane, methylene cyclopentane, propylcyclopentane, propylene cyclopentane and specific higher oligomers, depending on the nature of the heteroatomic ligand and the reaction conditions. A number of these products cannot be formed via conventional ethylene oligomerisation and trimerisation technologies in the yields observed in the present invention.

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preferable, depending on the further use of the product stream, to have such high selectivities of the α -olefin.

The olefinic feedstream may include ethylene and the $(C_6 + C_8) : (C_4 + C_{10})$ ratio in the product stream may be more than 2.5:1.

The olefinic feedstream may include ethylene and the $C_8 : C_6$ ratio in the product stream is more than 1.

The ethylene may be contacted with the catalyst system at a pressure of greater than 1 barg and preferably greater than 10 barg, more preferably greater than 30 barg.

The heteroatomic ligand may be described by the following general formula $(R)_nA-B-C(R)_m$ where A and C are independently selected from a group which comprises phosphorus, arsenic, antimony, oxygen, bismuth, sulphur, selenium, and nitrogen, and B is a linking group between A and C, and R is independently selected from any homo or heterohydrocarbyl group of which at least one R group is substituted with a polar substituent and n and m is determined by the respective valence and oxidation state of A and C.

A and/or C may be a potential electron donor for coordination with the transition metal.

An electron donor or electron donating substituent is defined as that entity that donates electrons used in chemical, including dative covalent, bond formation.

The heteroatomic ligand may be described by the following general formula $(R^1)(R^2)A-B-C(R^3)(R^4)$ where A and C are independently selected from a group which comprises phosphorus, arsenic, antimony, bismuth and nitrogen and B is a linking group between A and C, and R¹, R², R³ and R⁴ are independently selected from non-aromatic and aromatic, including heteroaromatic, groups of which at least one of R¹, R², R³ and R⁴ is substituted with a polar substituent.

In some embodiments of the process aspect of the invention, up to four of R¹, R², R³ and R⁴ may have substituents on the atom adjacent to the atom bound to A or C.

Claims

1. A process for tetramerisation of olefins wherein the product stream of the process contains more than 30% of the tetramer olefin.
2. A process as claimed in Claim 1 which process includes the step of contacting an olefinic feedstream with a catalyst system containing a transition metal compound and a heteroatomic ligand.
3. A process as claimed in Claim 1 or Claim 2, wherein the heteroatomic ligand is described by the following general formula $(R)_nA-B-C(R)_m$ where A and C are independently selected from a group which comprises phosphorus, arsenic, antimony, oxygen, bismuth, sulphur, selenium, and nitrogen, and B is a linking group between A and C, and the R's are the same or different and each R is independently selected from any homo or hetero hydrocarbyl group and n and m for each R is independently determined by the respective valence and oxidation state of A and C and of which at least one of the R's is substituted with a polar substituent.
4. A process as claimed in Claim 3, wherein the ligand comprises of multiples of $(R)_nA-B-C(R)_m$.
5. A process as claimed in any one of claims 1 to 3, which process includes the step of contacting an olefinic feedstream with a catalyst system which includes a transition metal and a heteroatomic ligand and wherein the tetramer is an olefin and makes up more than 30% of the product stream of the process and wherein the heteroatomic ligand is described by the following general formula $(R^1)(R^2)A-B-C(R^3)(R^4)$ where A and C are independently selected from a group which comprises phosphorus, arsenic, antimony, bismuth, and nitrogen and B is a linking group between A and C, and R¹, R², R³ and R⁴ are independently selected from non-aromatic and aromatic, including heteroaromatic, groups of which at least one of R¹, R², R³ and R⁴ is substituted with a polar substituent.

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6. A process as claimed in Claim 5, wherein up to four of R¹, R², R³ and R⁴ have substituents on the atom adjacent to the atom bound to A or C.
7. A process as claimed in Claim 5 or Claim 6, wherein each of R¹, R², R³ and R⁴ is aromatic, including heteroaromatic, but not all of R¹, R², R³ and R⁴ are substituted by any substituent on an atom adjacent to the atom bound to A or C.
8. A process as claimed in Claim 7, wherein not more than two of R¹, R², R³ and R⁴ have substituents on the atom adjacent to the atom bound to A or C.
9. A process as claimed in Claim 7 or Claim 8, wherein any polar substituents on R¹, R², R³ and R⁴ are not on the atom adjacent to the atom bound to A or C.
10. A process as claimed in any one of claims 5 and 7 to 9, wherein at least one of R¹, R², R³ and R⁴ is substituted with a polar substituent on the 2nd or further atom from the atom bound to A or C.
11. A process as claimed in any one of claims 3 to 5 and 7 to 10, wherein any polar substituents on one or more of R¹, R², R³ and R⁴ are electron donating.
12. A process as claimed in any one of claims 1 to 5 and 7 to 11, wherein the feedstream includes an α -olefin and the product stream includes at least 30% of a tetramerised α -olefin monomer.
13. A process as claimed in any one of claims 1 to 5 and 7 to 12, wherein the olefinic feedstream includes ethylene and the product stream includes at least 30% 1-octene.
14. A process as claimed in any one of claims 1 to 5 and 7 to 12, wherein the olefinic feedstream includes ethylene and the product stream includes at least 40% 1-octene.
15. A process as claimed in any one of claims 1 to 5 and 7 to 12, wherein the olefinic feedstream includes ethylene and the product stream includes at least 50% 1-octene.

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16. A process as claimed in any one of claims 1 to 5 and 7 to 12, wherein the olefinic feedstream includes ethylene and the product stream includes at least 60% 1-octene.
17. A process as claimed in any one of claims 1 to 5 and 7 to 16, wherein the olefinic feedstream includes ethylene and wherein the $(C_6 + C_8) : (C_4 + C_{10})$ ratio in the product stream is more than 2.5:1.
18. A process as claimed in any one of claims 1 to 5 and 7 to 17, wherein the olefinic feedstream includes ethylene and wherein the $C_8 : C_6$ ratio in the product stream is more than 1.
19. A process as claimed in any one of claims 12 to 18, wherein ethylene is contacted with the catalyst system at a pressure of more than 10 barg.
20. A process as claimed in any one of claims 3 to 5 and 7 to 19, wherein A and/or C are a potential electron donor for coordination with the transition metal.
21. A process as claimed in any one of claims 3 to 5 and 7 to 20, wherein B is selected from any one of a group comprising: organic linking groups comprising a hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl and a substituted heterohydrocarbyl; inorganic linking groups comprising single atom links; ionic links; and a group comprising methylene, dimethylmethylen, 1,2-ethane, 1,2-phenylene, 1,2-propane, 1,2-catechol, 1,2-dimethylhydrazine, $-B(R^5)-$, $-Si(R^5)_2-$, $-P(R^5)-$ and $-N(R^5)-$ where R^5 is hydrogen, a hydrocarbyl or substituted hydrocarbyl, a substituted heteroatom and a halogen.
22. A process as claimed in any one of claims 3 to 5 and 7 to 21, wherein B is selected to be a single atom spacer.
23. A process as claimed in any one of claims 3 to 5 and 7 to 22, wherein B is selected to be $-N(R^5)-$, wherein R^5 is hydrogen or selected from the groups consisting of alkyl, substituted alkyl, aryl, substituted aryl, aryloxy, substituted aryloxy, halogen, nitro, alkoxycarbonyl, carbonyloxy, alkoxy, aminocarbonyl, carbonylamino, dialkylamino, silyl groups or derivatives thereof, and aryl substituted with any of these substituents.

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24. A process as claimed in any one of claims 3 to 5 and 7 to 23, wherein A and/or C is independently oxidised by S, Se, N or O, where the valence of A and/or C allows for such oxidation.
25. A process as claimed in any one of claims 3 to 5 and 7 to 24, wherein A and C is independently phosphorous or phosphorous oxidised by S or Se or N or O.
26. A process as claimed in any one of claims 3 to 5 and 7 to 25, wherein R¹, R², R³ and R⁴ are independently selected from a group comprising a benzyl, phenyl, tolyl, xylol, mesityl, biphenyl, naphthyl, anthracenyl, methoxy, ethoxy, phenoxy, tolyloxy, dimethylamino, diethylamino, methylethylamino, thiophenyl, pyridyl, thioethyl, thiophenoxy, trimethylsilyl, dimethylhydrazyl, methyl, ethyl, ethenyl, propyl, butyl, propenyl, propynyl, cyclopentyl, cyclohexyl, ferrocenyl and tetrahydrofuranyl group.
27. A process as claimed in any one of claims 3 to 5 and 7 to 26, wherein R¹, R², R³ and R⁴ are independently selected from a group comprising a phenyl, toyl, biphenyl, naphthyl, thiophenyl and ethyl group.
28. A process as claimed in any one of claims 2 to 5, 7 to 23 and 25 to 27 wherein the ligand is selected from any one of a group comprising (3-methoxyphenyl)₂PN(methyl)P(3-methoxyphenyl)₂, (4-methoxyphenyl)₂PN(methyl)P(4-methoxyphenyl)₂, (3-methoxyphenyl)₂PN(isopropyl)P(3-methoxyphenyl)₂, (4-methoxyphenyl)₂PN(isopropyl)P(4-methoxyphenyl)₂, (4-methoxyphenyl)₂PN(2-ethylhexyl)P(4-methoxyphenyl)₂, (3-methoxyphenyl)(phenyl)PN(methyl)P(phenyl)₂ and (4-methoxyphenyl)(phenyl)PN(methyl)P(phenyl)₂, (3-methoxyphenyl)(phenyl)PN(methyl)P(3-methoxyphenyl)(phenyl), (4-methoxyphenyl)(phenyl)PN(methyl)P(4-methoxyphenyl)(phenyl), (3-methoxyphenyl)₂PN(methyl)P(phenyl)₂ and (4-methoxyphenyl)₂PN(methyl)P(phenyl)₂, (4-methoxyphenyl)₂PN(1-cyclohexylethyl)P(4-methoxyphenyl)₂, (4-methoxyphenyl)₂PN(2-methylcyclohexyl)P(4-methoxyphenyl)₂, (4-methoxyphenyl)₂PN(decyl)P(4-methoxyphenyl)₂, (4-methoxyphenyl)₂PN(pentyl)P(4-methoxyphenyl)₂, (4-methoxyphenyl)₂PN(benzyl)P(4-methoxyphenyl)₂, (4-methoxyphenyl)₂PN(phenyl)P(4-methoxyphenyl)₂, (4-fluorophenyl)₂PN(methyl)P(4-fluorophenyl)₂.

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fluorophenyl)₂PN(methyl)P(2-fluorophenyl)₂, (4-dimethylamino-phenyl)₂PN(methyl)P(4-dimethylamino-phenyl)₂, (4-methoxyphenyl)₂PN(allyl)P(4-methoxyphenyl)₂, (phenyl)₂PN(isopropyl)P(2-methoxyphenyl)₂, (4-(4-methoxyphenyl)-phenyl)₂PN(isopropyl)P(4-(4-methoxyphenyl)-phenyl)₂ and (4-methoxyphenyl)(phenyl)PN(isopropyl)P(phenyl)₂.

29. A process as claimed in any one of the claims 1 to 5 and 7 to 28, which process includes the step of combining in any order a heteroatomic ligand with a transition metal compound and an activator.

30. A process as claimed in any one of claims 2 to 5 and 7 to 28, which process includes the step of adding a pre-formed coordination complex, prepared using the heteroatomic ligand and a transition metal compound, to a reaction mixture containing an activator,

31. A process as claimed in Claim 30, which includes the step of generating a heteroatomic coordination complex *in situ* from a transition metal compound and a heteroatomic ligand.

32. A process as claimed in any one of the claims 2 to 5 and 7 to 31, wherein the transition metal is selected from any one of a group comprising chromium, molybdenum, tungsten, titanium, tantalum, vanadium and zirconium.

33. A process as claimed in any one of the claims 2 to 5 and 7 to 32, wherein the transition metal is chromium.

34. A process as claimed in any one of claims 29 to 31, wherein the transition metal compound is selected from a group comprising of an inorganic salt, organic salt, a co-ordination complex and organometallic complex.

35. A process as claimed in Claim 34, wherein the transition metal compound is selected from any one of a group comprising chromium trichloride tris-tetrahydrofuran complex, (benzene)tricarbonyl chromium, chromium (III) octanoate, chromium (III) acetylacetone, chromium hexacarbonyl and chromium (III) 2-ethylhexanoate.

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36. A process as claimed in any one of claims 29 to 31 and 33 to 35, wherein the transition metal compound is selected from a complex selected from chromium (III) acetylacetonoate and chromium (III) 2-ethylhexanoate.

37. A process as claimed in any one of claims 29 to 36, wherein the transition metal from a transition metal compound and heteroatomic ligand are combined to provide metal/ligand ratios from about 0.01:100 to 10 000:1.

38. A process as claimed in Claim 37, wherein the transition metal compound and heteroatomic ligand are combined to provide metal/ligand ratios from about 0.1:1 to 10:1.

39. A process as claimed in any one of claims 29 to 38, wherein the catalyst system includes an activator selected from any one of a group consisting of organoaluminium compounds, organoboron compounds, organic salts, such as methylolithium and methylmagnesium bromide, inorganic acids and salts, such as tetrafluoroboric acid etherate, silver tetrafluoroborate and sodium hexafluoroantimonate.

40. A process as claimed in any one of claims 29 to 31, wherein the activator is selected from alkylaluminoxanes.

41. A process as claimed in Claim 40, wherein the alkylaluminoxane, or mixtures thereof, is selected from group which consists of methylaluminoxane (MAO), ethylaluminoxane (EAO) and modified alkylaluminoxanes (MMAO).

42. A process as claimed in Claim 41, wherein the transition metal and the aluminoxane are combined in proportions to provide Al/metal ratios from about 1:1 to 10 000:1.

43. A process as claimed in Claim 42, wherein the transition metal and the aluminoxane are combined in proportions to provide Al/metal ratios from about 1:1 to 1000:1.

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44. A process as claimed in Claim 43, wherein the transition metal and the aluminoxane are combined in proportions to provide Al/metal ratios from about 1:1 to 300:1.
45. A process as claimed in any one of claims 42 to 44, which includes the step of adding to the catalyst system a trialkylaluminium compound in amounts of between 0.01 to 100 mol per mol of alkylaluminoxane.
46. A process as claimed in any one of claims 2 to 5 and 7 to 45, which includes the step of mixing the components of the catalyst system at any temperature between -20°C and 250°C in the presence of an olefin.
47. A process as claimed in any one of claims 2 to 5 and 7 to 46, wherein the product stream is contacted with the catalyst system at a temperature ranging between 15 and 130 °C.
48. A process as claimed in claims 1 to 5 and 7 to 47, wherein methylcyclopentane and methylene cyclopentane are formed as products and independently make up at least 1% of the product stream of the process.
49. A tetramerisation catalyst system which includes a transition metal and a heteroatomic ligand described by the following general formula $(R)_nA-B-C(R)_m$ where A and C are independently selected from a group which comprises phosphorus, arsenic, antimony, oxygen, bismuth, sulphur, selenium, and nitrogen, and B is a linking group between A and C, and the R's are the same or different and each R is independently selected from any homo or hetero hydrocarbyl group and n and m for each R is independently determined by the respective valence and oxidation state of A and C and of which at least one of the R's is substituted with a polar substituent.
50. A catalyst system as claimed in Claim 49, wherein the ligand comprises of multiples of $(R)_nA-B-C(R)_m$.
51. A catalyst system as claimed in Claim 49 or Claim 50 which includes a transition metal and a heteroatomic ligand described by the following general formula $(R^1)(R^2)A-B-$

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$C(R^3)(R^4)$ where A and C are independently selected from a group which comprises phosphorus, arsenic, antimony, bismuth, and nitrogen and B is a linking group between A and C, and R^1 , R^2 , R^3 and R^4 are independently selected from non-aromatic and aromatic, including heteroaromatic, groups of which at least one of R^1 , R^2 , R^3 and R^4 is substituted with a polar substituent.

52. A catalyst system as claimed in Claim 50 or Claim 51, wherein each of R^1 , R^2 , R^3 and R^4 is aromatic, including heteroaromatic, but not all of R^1 , R^2 , R^3 and R^4 are substituted by any substituent on an atom adjacent to the atom bound to A or C.

53. A catalyst system as claimed in Claim 51 or Claim 52, wherein not more than two of R^1 , R^2 , R^3 and R^4 have substituents on the atom adjacent to the atom bound to A or C.

54. A catalyst system as claimed in Claim 52, wherein any polar substituents on R^1 , R^2 , R^3 and R^4 are not on the atom adjacent to the atom bound to A or C.

55. A catalyst system as claimed in any one of claims 52 to 54, wherein at least one of R^1 , R^2 , R^3 and R^4 is substituted with a polar substituent on the 2nd or further atom from the atom bound to A or C.

56. A catalyst system as claimed in any one of claims 49 to 55, wherein any polar substituents on one or more of R^1 , R^2 , R^3 and R^4 are electron donating.

57. A catalyst system as claimed in any one of claims 49 to 56, wherein A and/or C are a potential electron donor for coordination with the transition metal.

58. A catalyst system as claimed in any one of claims 49 to 57, wherein B is selected from any one of a group comprising: organic linking groups comprising a hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl and a substituted heterohydrocarbyl; inorganic linking groups comprising single atom links; ionic links; and a group comprising methylene, dimethylmethylen, 1,2-ethane, 1,2-phenylene, 1,2-propane, 1,2-catechol, 1,2-dimethylhydrazine, - $B(R^5)-$, - $Si(R^5)_2-$, - $P(R^5)-$ and - $N(R^5)-$ where R^5 is hydrogen, a hydrocarbyl or substituted hydrocarbyl, a substituted heteroatom and a halogen.

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59. A catalyst system as claimed in any one of claims 49 to 58, wherein B is selected to be a single atom spacer.

60. A catalyst system as claimed in any one of claims 49 to 59, wherein B is selected to be -N(R⁵)-, wherein R⁵ is hydrogen or selected from the groups consisting of alkyl, substituted alkyl, aryl, substituted aryl, aryloxy, substituted aryloxy, halogen, nitro, alkoxycarbonyl, carbonyloxy, alkoxy, aminocarbonyl, carbonylamino, dialkylamino, silyl groups or derivatives thereof, and aryl substituted with any of these substituents.

61. A catalyst system as claimed in any one of claims 50 to 60, wherein A and/or C is independently oxidised by S, Se, N or O, where the valence of A and/or C allows for such oxidation.

62. A catalyst system as claimed in any one of claims 50 to 60, wherein A and C is independently phosphorus or phosphorus oxidised by S or Se or N or O.

63. A catalyst system as claimed in any one of claims 49 to 62, wherein R¹, R², R³ and R⁴ are independently selected from a group comprising a benzyl, phenyl, tolyl, xylyl, mesityl, biphenyl, naphthyl, anthracenyl, methoxy, ethoxy, phenoxy, tolyloxy, dimethylamino, diethylamino, methylethylamino, thiophenyl, pyridyl, thioethyl, thiophenoxy, trimethylsilyl, dimethylhydrazyl, methyl, ethyl, ethenyl, propyl, butyl, propenyl, propynyl, cyclopentyl, cyclohexyl, ferrocenyl and tetrahydrofuranyl group.

64. A catalyst system as claimed in any one of claims 49 to 63, wherein R¹, R², R³ and R⁴ are independently selected from a group comprising a phenyl, tolyl, biphenyl, naphthyl, thiophenyl and ethyl group.

65. A catalyst system as claimed in any one of claims 50 to 60 and 62 to 64 wherein the ligand is selected from any one of a group comprising (3-methoxyphenyl)₂PN(methyl)P(3-methoxyphenyl)₂, (4-methoxyphenyl)₂PN(methyl)P(4-methoxyphenyl)₂, (3-methoxyphenyl)₂PN(isopropyl)P(3-methoxyphenyl)₂, (4-methoxyphenyl)₂PN(isopropyl)P(4-methoxyphenyl)₂, (4-methoxyphenyl)₂PN(2-ethylhexyl)P(4-methoxyphenyl)₂, (3-methoxyphenyl)(phenyl)PN(methyl)P(phenyl)₂ and (4-methoxyphenyl)(phenyl)PN(methyl)P(phenyl)₂.

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methoxyphenyl)(phenyl)PN(methyl)P(3-methoxyphenyl)(phenyl), (4-
methoxyphenyl)(phenyl)PN(methyl)P(4-methoxyphenyl)(phenyl), (3-
methoxyphenyl)₂PN(methyl)P(phenyl)₂ and (4-methoxyphenyl)₂PN(methyl)P(phenyl)₂, (4-
methoxyphenyl)₂PN(1-cyclohexylethyl)P(4-methoxyphenyl)₂, (4-methoxyphenyl)₂PN(2-
methylcyclohexyl)P(4-methoxyphenyl)₂, (4-methoxyphenyl)₂PN(decyl)P(4-
methoxyphenyl)₂, (4-methoxyphenyl)₂PN(pentyl)P(4-methoxyphenyl)₂, (4-
methoxyphenyl)₂PN(benzyl)P(4-methoxyphenyl)₂, (4-methoxyphenyl)₂PN(phenyl)P(4-
methoxyphenyl)₂, (4-fluorophenyl)₂PN(methyl)P(4-fluorophenyl)₂, (2-
fluorophenyl)₂PN(methyl)P(2-fluorophenyl)₂, (4-dimethylamino-phenyl)₂PN(methyl)P(4-
dimethylamino-phenyl)₂, (4-methoxyphenyl)₂PN(allyl)P(4-methoxyphenyl)₂,
(phenyl)₂PN(isopropyl)P(2-methoxyphenyl)₂, (4-(4-methoxyphenyl)-phenyl)₂ and (4-
methoxyphenyl)(phenyl)PN(isopropyl)P(phenyl)₂.

66. A catalyst system as claimed any one of the claims 49 to 65, wherein the transition metal is selected from any one of a group comprising chromium, molybdenum, tungsten, titanium, tantalum, vanadium and zirconium.

67. A catalyst system as claimed in any one of the claims 49 to 66, wherein the transition metal is chromium.

68. A catalyst system as claimed in Claim 67, wherein the transition metal is derived from a transition metal compound selected from a group comprising of an inorganic salt, organic salt, a co-ordination complex and organometallic complex.

69. A catalyst system as claimed in Claim 68, wherein the transition metal compound is selected from a group comprising chromium trichloride tris-tetrahydrofuran complex, (benzene)tricarbonyl chromium, chromium (III) octanoate, chromium (III) acetylacetoneate, chromium hexacarbonyl, and chromium (III) 2-ethylhexanoate.

70. A catalyst system as claimed in any one of claims 49 to 69, wherein the transition metal is selected from a complex selected from chromium (III) acetylacetoneate and chromium (III) 2-ethylhexanoate.

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71. A catalyst system as claimed in Claim 68 or Claim 69, wherein the transition metal from a transition metal compound and heteroatomic ligand are combined to provide metal/ligand ratios from about 0.01:100 to 10 000:1.
72. A catalyst as claimed in Claim 71, wherein the transition metal compound and heteroatomic ligand are combined to provide metal/ligand ratios from about 0.1:1 to 10:1.
73. A catalyst system as claimed in any one of the claims 49 to 72, which includes an activator.
74. A catalyst system as claimed in Claim 73, wherein the activator is selected from any one of a group consisting of organocalcium compounds, organoboron compounds, organic salts, such as methyl lithium and methylmagnesium bromide, inorganic acids and salts, such as tetrafluoroboric acid etherate, silver tetrafluoroborate and sodium hexafluoroantimonate.
75. A catalyst system as claimed in Claim 73 or Claim 74, wherein the activator is selected from alkylaluminoxanes.
76. A catalyst system as claimed in Claim 75, wherein the alkylaluminoxane, or mixtures thereof, is selected from group which consists of methylaluminoxane (MAO), ethylaluminoxane (EAO) and modified alkylaluminoxanes (MMAO).
77. A catalyst system as claimed in Claim 75 or Claim 76, wherein the transition metal and the aluminoxane are combined in proportions to provide Al/metal ratios from about 1:1 to 10 000:1.
78. A catalyst system as claimed in Claim 77, wherein the transition metal and the aluminoxane are combined in proportions to provide Al/metal ratios from about 1:1 to 1000:1.

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79. A catalyst system as claimed in Claim 78, wherein the transition metal and the aluminoxane are combined in proportions to provide Al/metal ratios from about 1:1 to 300:1.
80. A catalyst system as claimed in any one of claims 75 to 79, which includes a trialkylaluminium compound in amounts of between 0.01 to 100 mol per mol of alkylaluminoxane.
81. Use of a tetramerisation catalyst system as claimed in any one of claims 49 to 80 for the tetramerisation of olefins.
82. Use of a tetramerisation catalyst system as claimed in any one of claims 49 to 80 for the tetramerisation of ethylene.
83. Use of a ligand for a tetramerisation process as claimed in any one of claims 1 to 5 and 7 to 48.
84. Use of a ligand for a tetramerisation catalyst system as claimed in any one of claims 49 to 80.
83. An olefin tetramerisation process substantially as described herein.
84. An olefin tetramerisation catalyst system substantially as described herein.

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